SUGARY WAYS TO MAKE NANOTUBES DISSOLVE

Starch, gum arabic, and glucosamine allow carbon nanotubes to slip into aqueous solution

RON DAGANI, C&EN WASHINGTON

Spitting is not considered out of bounds in J. Fraser Stoddart's lab--as long as it advances the science.

So when Stoddart, a chemistry professor at the University of California, Los Angeles, encouraged postdoctoral fellow Alexander Star to spit into an aqueous solution of starch-wrapped carbon nanotubes, it was to see whether the α-amylase in saliva would chop the amylose chains of starch into pieces, thus releasing the nanotubes and causing them to precipitate from solution. That is indeed what happened, providing additional evidence that the chemists had succeeded in solubilizing nanotubes by encircling them with starch molecules.

Stoddart's group is one of several that have recently turned to natural carbohydrates to overcome one of the major practical problems of carbon nanotubes--their extreme insolubility. The insolubility of nanotubes makes it more difficult to purify them, separate them according to length or other characteristics, chemically modify their surfaces, and develop applications for them.

In recent years, chemists have explored several strategies--both covalent and noncovalent--to functionalize single-walled nanotubes (SWNTs) so as to improve their solubility. A noncovalent strategy that preserves the unique physical properties of the nanotubes is to wrap them in polymer chains. Stoddart's lab and many others have previously shown that synthetic polymers can alter the nanotubes' chemical properties and render them soluble in organic solvents (C&EN, May 7, 2001, page 15).

But if scientists are to seriously consider exploiting the unique properties of nanotubes in a biological setting, they will likely...
want to make these graphitic tubules soluble in aqueous media. Some polymers and surfactants have already been shown to improve the solubility of SWNTs in aqueous solutions, but these materials may not be as biocompatible as would be desired, according to Stoddart and coworkers.

"It was for this reason, amongst others, that we decided to explore the possibility of solubilizing SWNTs in aqueous solutions of starch," the researchers write in the latest edition of *Angewandte Chemie International Edition* [41, 2508 (2002)]. Stoddart, who began his career as a carbohydrate chemist, knew that cyclodextrins (the macrocyclic analogs of starch) had been used to render fullerenes like C_{60} soluble in water. So why not use common starch to solubilize nanotubes?

**IN STAR'S INITIAL** experiments, it didn't work: An aqueous solution of starch failed to dissolve SWNTs. However, when Star tried an aqueous solution of a starch-iodine complex, the nanotubes did dissolve. The researchers' explanation for this finding involves amylose--the linear, unbranched component of starch that consists of d-glucose units connected via \( \alpha,\beta \)-glycosidic linkages. When an amylose strand encounters certain small molecules such as those of iodine, it forms a left-handed helix that coils around the small molecules. This complexation sets the stage for a carbon nanotube or nanotube bundle to come along and displace the small guest molecules inside the helix via a "pea-shooting" type of mechanism, Stoddart says.

In support of this explanation, Star found that, in water, an amylose-iodine complex works just about as well as a starch-iodine complex in solubilizing SWNTs. Most starches are only 10 to 20% amylose, with the remaining 80 to 90% consisting of amylopectin, a branched, dendrimer-like polymer of d-glucose. An aqueous amylopectin-iodine complex was found not to dissolve SWNTs, however. These results suggest, therefore, that amylose is largely responsible for starch's nanotube-solubilizing capability, although the presence of amylopectin seems to enhance it.

Stoddart and Star's UCLA collaborators--chemistry professor James R. Heath and graduate student David W. Steuerman--examined the dried, starched SWNTs by atomic force microscopy. The images reveal small bundles of nanotubes that are "covered profusely with amorphous polysaccharide," according to the team's paper.

Star and Stoddart found that aqueous solutions of starch-wrapped SWNTs are stable for weeks, "provided you do not spit on them!" Addition of saliva leads to precipitation of the nanotubes after several hours, they note. Even quicker precipitation--within 10 minutes--can be achieved by adding amyloglucosidase, a commercially available enzyme that
hydrolyzes starch.

THESE FINDINGS suggest a new method for purifying SWNTs cheaply and under ordinary conditions using readily available starch complexes, the chemists point out. The protocol involves dissolving impure SWNTs in water with starch-iodine complex, removing undissolved impurities by centrifugation, and then precipitating the starch-wrapped tubes by boiling the solution. The starched SWNTs are redissolved in water, incubated with amyloglucosidase, and then the precipitated nanotubes are removed by filtration and washed with water.

According to Stoddart, it's unclear whether the starch strands are coiled mostly around bundles of aligned nanotubes ("ropes")--the usual form in which SWNTs are produced--or whether the polysaccharide can also separate these bundles into individual SWNTs before wrapping. Such a capability, which would be very useful, has, in fact, been demonstrated recently with a different water-soluble polysaccharide.

At Ben Gurion University of the Negev, in Beer Sheva, Israel, researchers in the chemical engineering department and the Ilse Katz Center for Meso & Nanoscale Science & Technology have found that they can separate nanotube ropes into individual tubes and disperse these in aqueous solutions using gum arabic, a complex polysaccharide exuded by Acacia Senegal trees [Nano Lett., 2, 25 (2002)]. Gum arabic is a highly branched glycopolymer containing galactose, rhamnose, arabinose, and glucuronic acid as the calcium, magnesium, and potassium salts. It has been known since ancient times and is widely used in foods and beverages as an emulsifier, stabilizer, and thickener, among other uses.

The Israeli team--consisting of professor Oren Regev, senior lecturer Rachel Yerushalmi-Rozen, postdoc Rajdip Bandyopadhyaya, and graduate student Einat Nativ-Roth--describe using a dispersion method based on an ancient Egyptian recipe, first used 5,000 years ago to prepare carbon-black ink. Essentially, they dissolve gum arabic in water, add as-produced nanotubes (which contain carbon and metal impurities), and sonicate the mixture very gently (so as not to break the tubes). This procedure yields a homogeneous, inklike suspension that is stable for months. The suspension can be dried and reconstituted with water. Alternatively, the gum arabic in the dry dispersion can be burned off without affecting the properties of the nanotubes, according to Yerushalmi-Rozen.

Based on results from X-ray scattering experiments and transmission electron microscopy, the researchers believe that gum arabic molecules adsorb to nanotube ropes and, through repulsive forces between the adsorbed polymer chains, prevent individual tubes from reaggregating after they have
separated from the bundle during the sonication step. Once this repulsive barrier is set, Yerushalmi-Rozen explains, the dispersion of individual nanotubes becomes thermodynamically stable.

"Individual nanotubes have much better mechanical and electronic properties than ropes," she points out, "and their processing should be much easier." Individual nanotubes also would be preferred for making many types of nanocomposites. The researchers suggest, for example, that the gum arabic molecules that adsorb to the nanotubes may help the tubes to adhere to a polymeric matrix, which could result in stronger, tougher nanotube-polymer composites.

**WHILE COMPLEX** polymeric molecules made from sugar building blocks can interact noncovalently with SWNTs to solubilize or disperse the tubes in water, simple monosaccharides can do the same through covalent bonding. This was demonstrated recently at the University of Oklahoma, Norman, by Francisco Pompeo, a research associate working in the laboratory of Daniel E. Resasco, a professor of chemical engineering and materials science. They used glucosamine, a natural amino sugar that has come into the public eye in recent years as a widely touted remedy for osteoarthritis pain.

The Oklahoma scientists chose glucosamine because it is highly soluble in water and contains an amine group, which can easily be attached to a SWNT. They followed a standard procedure to generate SWNTs having acyl chloride substituents, which react with the sugar's amine group to form an amide bond. The grafted glucosamine units were found to solubilize the nanotubes in water, as judged by the fact that the resulting solutions remain translucent and homogeneous for weeks [Nano Lett., 2, 369 (2002)]. The glucosamine-grafted nanotubes—though much less soluble than glucosamine itself—have solubilities comparable to those reported for functionalized SWNTs in organic solvents, Resasco notes.

This approach might also be used, for example, to link a nanotube to a DNA sequence that would bind specifically to a protein in a cancer cell, he says. Grafting a cell toxin to another part of the same nanotube might provide a tailorable "guided missile" that could home in on tumor cells and destroy them.

Still, there's something appealing about the idea of coaxing normally hydrophobic nanotubes into water by sheathing them in a natural, water-soluble polymer. This approach preserves the nanotube's physical properties in a biocompatible, environmentally friendly way. So it's no surprise that Stoddart says, "I'm sure we're going to see more examples of natural polymers—including proteins and nucleic
acids--being used to solubilize carbon nanotubes in water."