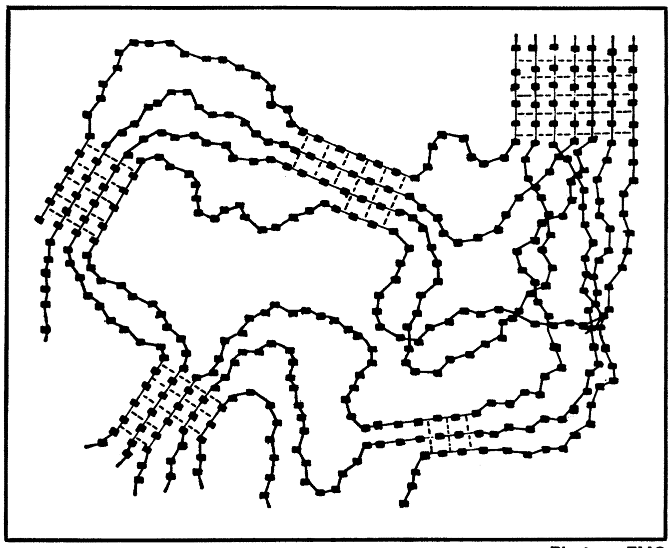
POLYMER CHEMISTRY

Bright future for a serendipitous chemical discovery



Photos: FMC

Microcrystals are formed within the high polymers.

Microcrystalline polymers are finding an increasing number of scientific and commercial uses

by Edward Gross

In 1955, when polymer chemists proceeding along conventional lines were making new plastic, rubber and textile compositions, a radically different type of material was discovered: colloidal microcrystalline polymers. In the 15 years since that discovery, these polymers have slowly been developed; several products are now on the market, and more are in the offing.

The microcrystallines are a man-made state of colloids composed of crystals 25 to 5,000 angstroms in length: the size of viruses and bacteria. Before 1955 single polymer crystals were a laboratory phenomenon studied largely with the electron microscope. The discovery that they could be made into a useful material is a tale of scientific serendipity.

Dr. O. A. Battista at American Viscose Division of FMC Corp. in Marcus Hook, Pa., was trying to make a stronger rayon tire cord by breaking down cellulose into tiny crystals that would precipitate the cellulose molecules in the viscose solution into a more ordered structure. Instead, what he got was a gel that looked like white petroleum jelly. Electron microscopy revealed that the new gel was made of tiny crystals in the colloidal size range—somewhere between the size of flu and wart viruses—suspended in water along with much larger particles which comprised bundles of the single free microcrystals.

The planned experiment for tire cord was shelved because of the other potentialities opened up by the new material's unique properties. The properties, such as high viscosity, heat resistance and water miscibility, were imparted to it by the colloidal size of the microcrystals.

Although the material was new, polymer chemists had been aware of the existence of polymer microcrystals for many years. But they only studied them as a collection of hundreds of molecules in a polymer matrix. Now they existed freed, as highly concentrated colloidal particles suspended in a water-based gel.

"Scientists had been preoccupied with putting polymers in solution so they could spin fibers and films from them," explains Dr. Battista. "After making the first practical colloidal microcrystalline cellulose gels, we deliberately stopped at precise colloidal dimensions with subsequent polymers that gave similar products with commercial utility."

Four new products based on polymer microcrystals were being marketed by 1969. Now three more are emerging from the laboratory, understanding of them is accumulating and a new field of colloidal polymer science is developing.

These new polymers have been working their way into pharmaceuticals, cosmetics, foods, coatings and epoxy resins. Because they still represent a relatively new technology, they are also of interest for scientific investigations in a number of areas, which include water pollution, cloud seeding and superconductivity.

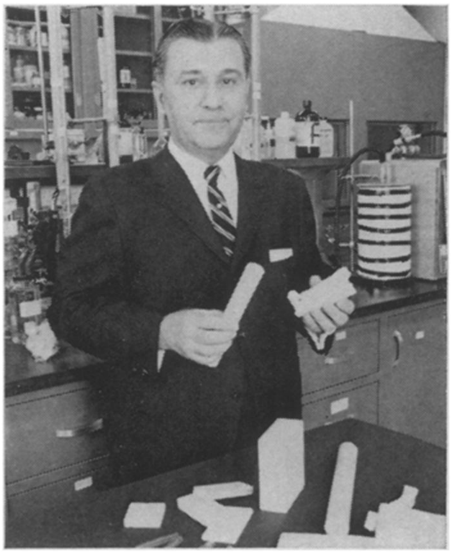
The starting material for each product is a high molecular-weight polymer, a compound composed of very long-chain molecules. When these molecules crystallize out of solution, they pack together and some parts of them line up side by side like matchsticks, into orderly areas, or microcrystals, while other parts of the same molecules kink up between the microcrystals to produce areas of disorder or hinges.

The trick is to cut, etch or otherwise unhinge the regions between microcrystalline areas without destroying the microcrystals, a process analogous to dissolving the motar between bricks. Then a sufficient number of the microcrystals must be freed in water to produce the new colloidal polymer gels. If too few are freed, a useless sand-in-water type mixture results. The unhinging is usually done by a specific chemical, whose attack varies for each type of polymer. Mechanical agitation from a device, such as a blender, is used to assist in separating microcrystals that stick together.

Present research at FMC, the patent owner, is aimed at finding the optimum conditions, including temperature, pressure and chemical severity, needed to produce new species.

At present, there are seven types of colloidal microcrystalline polymers, five of which are in the commercial, semi-commercial or market development stage. Each take three forms: gel, powder and cream.

- Avicel, the first, is made of cellulose. It is the only fully commercial microcrystalline polymer, selling in the millions of pounds per year. Since it can be made into a gel that will not melt, it is used as a base for canned tuna salads and hollandaise sauce, whose oils normally would separate out when heat-sterilized. In the form of a free-flowing powder, it acts as a binding agent; each year millions of pounds of it are used in making drug tablets, its main application.
- Then there is Aviamylose, a microcrystalline starch, which offers possibilities similar to Avicel, but which is waiting for the right commercial time to debut.
- Avibest is a microcrystalline product of the mineral chrysotile asbestos. It is being used in polyester and epoxy resins to control their flow properties.
- Avitene, number four, is a microcrystalline form of collagen, a natural polymer that is the chief constituent of connective tissue and bone and is being



Battista with prostheses samples.

explored for its medical potential.

One such application is synthetic bone. Crystals of apatite, the chief mineral constituent of bone, can be incorporated into Avitene compositions, which can be fashioned into bone and cartilage-like shapes with characteristics almost identical to normal bone. "This new product has promising potential, but it's too early to predict its ultimate success," says Dr. Merritt R. Hait of St. Luke's Hospital Center in New York, where some of the experimental work on Avitene's medical applications is centered.

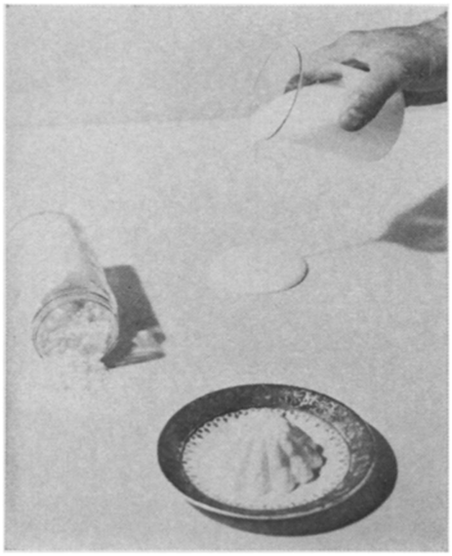
Last October, researchers at St. Luke's reported success with Avitene as a biological dressing. Porous mats of the polymer impregnated with antibiotics were placed over infected wounds in rabbits, and substantially faster healing was observed.

More spectacularly, Avitene has been successful in animal tests as a novel blood-clotting agent and adhesive for sutureless surgery. Gaping wounds were made in the liver and spleen and other vital organs, including the heart, stomach and major blood vessels, of more than 30 dogs. Avitene flour was packed in the wounds and the bleeding quickly stopped, without suturing.

As Dr. Hait sees Avitene, "It is going to reduce the amount of suturing required. It is also effective in massive hemorrhage where an organ or tissue integrity has been destroyed and suturing is ineffective or impossible."

Avitene has received a preliminary safety clearance from the Food and Drug Administration, and animal studies are under way.

▪ The last of the five marketable microcrystalline polymers is Aviamide, a microcrystalline nylon. It is being developed for coating textile glass fibers, thus permitting easier dyeing of fiber glass fabrics. Also it can coat metals



Forms of microcrystalline cellulose.

and provide a cheaper and quicker method of electrical insulation or weathering protection.

▪ The two newest additions to the microcrystalline polymer family are Aviester, which is microcrystalline polyester, and Aviolefin, made of polypropylene. These are in the laboratory stage and not yet available commercially. However, as with Aviamide, they too could coat metals and glass.

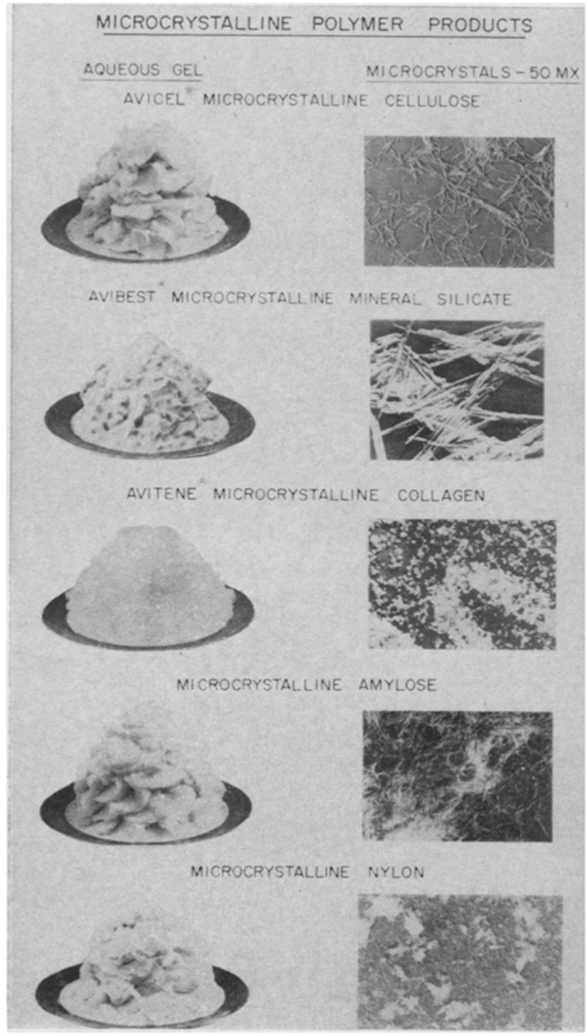
Because microcrystalline polymers are a new branch of colloidal polymer chemistry, there are many applications for them as yet untouched. "From what we see in their unique functional properties, they are bound to find a place in the whole realm of colloidal chemistry," sums up FMC's Dr. Battista, now assistant director of the company's central research department at Princeton, N.J.

Because they are hygroscopic (water attracting) to varying degrees, for example, they might be used to separate out water pollutants and microorganisms. "I believe some of these microcrystalline products will ultimately be used as absorbents to remove viruses and bacteria selectively, as well as other water contaminants," predicts Dr. Battista.

And because of their absorbency and smooth salve-like properties, they are finding increasing use in cosmetics. Avitene, for example, when added to a cologne or perfume, converts it into a cream or ointment which can then be dispensed from foil packet or plastic tube.

The same idea has been adopted for alcohol. A microcrystalline gel would contain the alcohol and could be rubbed on the skin, reducing the need for bottled rubbing alcohol.

Another area where the polymers might make some valuable input is in superconductivity, or the elimination of



The first five marketable products.

electrical resistance. Present superconductors work close to absolute zero. A goal of some chemists and physicists (SN: 9/20, p. 251) is to make superconducting plastics that could work at temperatures closer to room temperature. Scientists have come up against a stone wall in making them, but some researchers believe that single colloidal microcrystals, because of their size, could help solve the problem by filling gaps to convey electrons.

Another speculative research area is cloud seeding. Because of the range of polymer microcrystals now available, the possibility exists of engineering surface charges and sizes to produce seeding crystals that could attract water vapor to form raindrops. Such products have shown promise in cloud-chamber experiments.

Microcrystalline polymer partisans of research see more in the future than in the past. Says Dr. Battista: "Fifteen years of research with polymer microcrystals has done nothing but continue to build up our excitement over the promise of this new branch of polymer chemistry. Much unexplored territory lies ahead." □