

The Next Polymer Revolution

High polymers are now becoming part of inorganic chemistry

BY DIETRICK E. THOMSEN

There was a time when crockery was usually made of breakable glass or ceramics, fur coats came from endangered species, leather upholstery carried the aroma of the short-grass plains and the wearing of silk underwear was considered an effete custom of the sybaritic rich. It is hard to remember that time.

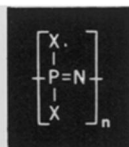
We all know, or we should know, that those creatures of the modern bestiary, the ever abundant nauga and the inexhaustible acrylic seal, originate not in the grassy veld of Africa or the icy waters of Kamchatka, but in the test tubes of the chemical laboratory, where petrochemicals are transformed into the products of today's civilization. From nylon and other polyester fabrics to handheld electronic calculators and magnetic tapes, life would hardly be the same without the assortment of modern synthetic materials around us.

Like all the other artifacts of the synthetic and plastic revolution—it is by no means too trite to use that word here—they are based on high polymers, a class of chemical compound that, like the biochemical substances its members so often replace, depends on the ability of carbon to bind with itself in long chains and complicated rings.

Conventional wisdom has it that the high polymer revolution is about over. Chemists have made just about all the compounds they can on the present basis.

Not so, says chemist Harry R. Allcock of Pennsylvania State University. More than a decade of work with a new and different sort of polymer, polymers with inorganic backbones, convinces him that a new revolution based on inorganic polymers is about to start.

What is wrong with our present array of synthetic organic polymers? Flammability comes first on Allcock's list of their deficiencies. This is a natural consequence of their being organic. Other detriments are also consequences of organic composition: They melt, or oxidize and char at high temperatures in the atmosphere. Few remain flexible at low temperatures. Many soften, swell or dissolve in gasoline, jet fuel or other hydrocarbons, and it is not difficult to see how that limits their uses. In addition, there is the biological factor. Much has been heard about the use of plastics in making artificial organs, pieces of blood vessel and so on. But many organic polymers initiate blood clotting or



The basic polyphosphazene unit is repeated many times. X represents any of the many possible substituents. Pictured are rubbery, fibrous and filmy examples of the inorganic breed.

generate toxic, irritant or carcinogenic responses. And the organic polymers are made from petroleum products, so reliance on a continuing abundant supply is a bit hazardous.

The inorganic polymers tend to avoid these disadvantages. Some of those that Allcock and his colleagues have developed at the Penn State laboratory are being mixed with other fibers to serve as flame retardants. Some of them seem especially promising for the fabrication of synthetic body parts.

In one sense, polymers with inorganic backbones are nothing strikingly new. Silicone polymers based on chains of silicon and oxygen molecules have been around since the 1940s and as Allcock puts it: "Silicone rubber is now used in applications for which stability, flexibility and biomedical compatibility are needed." Another recently developed

class of inorganic polymers is based on chains with alternating siloxane and carborene units.

The ones that Allcock and his collaborators have been working on, the polyphosphazenes, are of particular interest because they show a wide variety of possible compounds with a large selection of characteristics, which in many cases avoid the important detriments of organic polymers. Since the work started in 1965, more than 60 new polymers have been made. "They now constitute a substantial class of new elastomers, thermoplastics and fibers that promise to solve many of the technological and biomedical problems," Allcock says.

This class is based on a backbone of phosphorous and nitrogen atoms. The trick to polymerizing it is to break open the cyclic trimer, a closed ring containing three of the backbone combinations with which it starts, straighten the backbone so that more backbone pieces can be added and substitute various atoms and groups of atoms for the chlorine atoms that stick to the corners of the original trimer. The first attempts to do this were unsuccessful in producing polymers that do not react with water, but Allcock and colleagues noticed that the polymerization process took place in two steps. In the second step, they were able to substitute elements and groups of elements for the chlorine that rendered the resulting polymers stable in water.

The polymers they have made have molecular weights that sometimes exceed three and four million, indicating backbone chains at least 15,000 units long. A particularly exciting thing that became clear soon after the first successful substitutions were made was that different substituent groups made a "marked" difference in the properties of the polymers. Some substituents, such as methoxy and ethoxy, yield low-temperature elastomeric properties. Others (phenylamino, dimethylamino) give glassy polymers. Still others give flexible film-forming materials. All are stable in water bases or aqueous acids. "A quick consideration of the vast choice of different alcohols, and primary or secondary amines that are available to chemists illustrates that the unique advantage of polyphosphazenes is the ease with which a large variety of polymers, all with different properties, can be made from one precursor," Allcock writes in the Sept. 24 SCIENCE.

The first polyphosphazene polymers produced in Allcock's laboratory were homopolymers, which are made by substituting only one chemical group for the chlorine atoms bound laterally to the vertebrae of the polymer backbone. Many of these can be made into fibers, tubes and films, and because they do not burn, one of their first uses was to be mixed into fabrics as flame retardants.

But homopolymers have a certain det-

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uses this as a tool to screen pain patients and later on as a method to induce hypnosis. The two primary components of the HIP are the eye roll and arm levitation. Each is given a score from 0 to 4 and the average of the two is the profile score. An entire profile is complete when the patient has similar eye roll and arm levitation scores. Under some circumstances, only the eye roll is given. The patient is asked to roll the eyeballs up and look at the examiner's finger placed in the middle of the patient's forehead. The amount of white (schlera) showing as the patient closes the eyes is an effective statement of the person's receptivity to hypnosis. This test, used in conjunction with information derived from detailed, personal interviews with the patient, establishes what tactic will be used by the therapist in helping the patient to pain relief.

"Whether it's physical or psychosomatic pain," Wain says, "I can develop a strategy based on what the patient tells me about himself. He may tell me that he likes to go to church, or likes to sail boats. I may use this with him in therapy." Migraine headaches seem to be the condition most responsive to hypnotic suggestion. He has treated several patients in a relatively short time by suggesting that they imagine their heads feeling very cool and their hands becoming warm. Through repeated suggestions of various positive sensory projections many different types of pain are relieved or alleviated.

There is no moment of hesitation as to what he wants to achieve with each patient, besides the obvious control of their pain. "Helping them to develop techniques so that they can eventually help themselves . . . to make them dependent on themselves." Weaning the person from reliance on painkilling drugs makes for success as he sees it. "In time, I just change the prescription from medication to autohypnosis," he says, "and I might prescribe autosuggestion four times daily, for example . . .", depending on the case.

As in many areas of behavioral science, or the physical sciences for that matter, the reasons for success and data that satisfactorily substantiate the results are less than apparent. Perhaps the clinic's projected research will fill in the gaps. For now, Wain considers the clinicians to be far ahead of the laboratory researchers in understanding and collecting data and achieving results in hypnotic reduction of pain. There are far more psychological variables present in the clinics, since the pain is not simulated nor artificially induced, which can be learned from. But he does offer an insight into how many people actually find relief with hypnotic pain control. "Every patient gets the minimal amount of relief. If you give a person relaxation, pain will be decreased as well." Although every patient isn't able to get off all the medication, "quite a few have." □

. . . Inorganic Polymers

perimental quality, the susceptibility to formation of microcrystals. Polymeric molecules do not form crystals as a whole, but microcrystalline regions in a sample of homopolymer can crosslink adjacent strands, and these microcrystalline regions degrade the polymer's stretchability. Microcrystallization can be avoided by substituting more than one kind of chemical group for the chlorines that bind to the polyphosphazene backbone. This reduces the possibility of crosslinks because it is likely to put different chemical groups adjacent to each other. Techniques for this multiple substitution have been developed, and they produce extremely rubbery substances.

Of all the possible uses for polyphosphazene polymers, Allcock seems keenest about the biomedical developments. Many of these polymers are extremely hydrophobic—resistant to wetting by water. This makes them especially appropriate for use in artificial organs since they do not interfere with the physiological chemistry going on around them nor do they initiate unwanted reactions such as blood clotting.

More exotic is the possible use of polyphosphazene polymers as carriers for therapeutic agents. For example, it has been shown that square planar platinum complexes are powerful anticancer drugs. □

But they are small molecules and therefore rapidly excreted through the kidneys. Some of the polyphosphazenes are soluble in water (though not reactant with it). If the platinum compounds could be bound to these big, but not physiologically active molecules, they might stay in the body long enough to do some good.

Nature seems to do just this sort of thing. Many large proteins seem to serve mainly as carriers for metal atoms. The metals do the real physiochemical work, and the proteins seem to be there mainly to retard excretion of the metals or to prevent metal atoms from getting too close to each other to do their job. Hemoglobin seems a good example of this. It is the iron atoms in the hemoglobin that bind the oxygen and carry it around. The rest of this large and complicated protein seems to serve mainly as a carrier for the iron. Some polyphosphazenes could serve as artificial performers of this sort of function, and they may be useful in fundamental studies of the physiological activities of such proteins.

So it seems that we are on the way to a second polymer revolution. It appears to be one that is likely to provide as many wonders as the first, and its products may find their way into our bodies in functions where organic polymers, by the irony of their own organic nature, cannot properly serve. □



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