approximately 0.5 percent. Additional samples will be required, however, before it can be determined whether the Apollo 12 chromites are typical of lunar chromites.

The discovery of chromite and zircon crystals in a Muong Nong–type tektite increases the number of relict minerals now known to occur in tektites. The absence of any signs of decomposition of zircon or chromite to baddeleyite or eskolaite, respectively, supports previous observations which indicate that the Muong Nong–type tektites were less intensely heated than other tektite groups. X-ray asterism studies of the chromite and zircon crystals support an impact origin for the Muong Nong–type tektite. The presence of chromite and zircon together and the rounding of the crystals, along with evidence of sorting, all indicate that a sedimentary deposit is the source material for the Muong Nong–type tektite.

*Note added in proof*: After the above investigation was completed, corundum, rutile, and monazite, as well as quartz and zircon, have been tentatively identified by x-ray diffraction in another specimen of Muong Nong–type tektite from Indochina. These inclusions will be discussed in detail in a later publication.

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19. I thank Dr. J. A. O'Keefe for helpful suggestions and encouragement. C. W. Kouns and Chris Inman prepared the samples and helped with the photography. F. Wood, Jr., and W. Riffle helped with electron microprobe and x-ray analyses, respectively. Discussions with Drs. J. A. O'Keefe, H. O. A. Meyer, S. K. Saxena, and L. S. Walter have been helpful. Prof. V. E. Barnes, Drs. B. M. French, R. S. Clarke, Jr., and P. D. Lowman critically reviewed the manuscript. Judith A. Glass helped prepare the manuscript. The research was done while B.P.G. was on active duty with the U.S. Army Corps of Engineers assigned to Goddard Space Flight Center.

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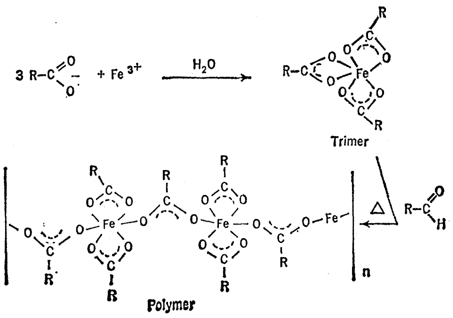
# Water-Degradable Polymers for Controlled Release of Herbicides and Other Agents

Abstract. *A new class of polymeric substances that degrade in the presence of water are formed by the reaction of carboxylic acids with metal ions in the presence of an aldehyde catalyst. Possible uses may be found in agricultural chemicals, packaging, and medicine. Important antipollution aspects are present in many of these applications.*

We have found that water-degradable polymers can be formed by the addition of a carboxylic acid and a metal ion in the presence of an aldehyde catalyst. On exposure to water, these polymers depolymerize more or less slowly to release the original carboxylic acid and the hydrous metal oxide gel. The substance whose controlled release is sought may itself be a carboxylic acid, as in the herbicide 2,4-D (*1*), or the substance may be dissolved in a water-degradable polymer formed with any convenient carboxylic acid plus metal. In either case, the desired substance is released on contact with water at a controlled rate which can be varied from days to years.

Water-degradable polymers may have been prepared previously but without an appreciation for the water-degradability. In 1904, for example, Joannis (*2*) prepared a copper benzoate "salt" which did not crystallize well. Purposeful attempts to form polymers incorporating metals have not been very successful. Pitts and Hurley (*3*) have sought unsuccessfully to polymerize bidentate and other ligands with aluminum, cadmium, and nickel. To the best of our knowledge, then, these unique materials are described here for the first time.

The structures and molecular weights of these polymers have not yet been determined. The polymers are thermoplastic and are not cross-linked, as they dissolve wholly in organic solvents such as acetone and methyl ethyl ketone. A proposed structure is:



On heating, the sticky resin is changed into a hard, glassy material which breaks with conchoidal fracture. Metals other than iron which yield these polymers include cobalt, copper, nickel, titanium, manganese, and chromium. The nature of the R-group on the aldehyde is not critical. However, it has been found that if the R-group on the aldehyde is similar to the R-group on the acid, the reaction proceeds more readily.

For example, 2-4-D was polymerized with ion as follows. To an aqueous solution of 3 moles of the amine salt of 2,4-D, sufficient nitric acid was added to lower the *p*H of the solution to about 4. An aqueous solution containing 1 mole of ferric nitrate and 2 ml of concentrated cinnamic aldehyde, in which some nitric acid was included to assist the dissolution of ferric nitrate, was also prepared. The ferric nitrate solution was added to the amine solution quickly after the *p*H of 4 was reached to preclude precipitation of 2,4-D. The addition of the ferric nitrate solution resulted in a further reduction of the *p*H to 3. Stirring of the combined solution at room temperature resulted in the formation of a precipitate in the form of a resinous, tacky composition which settled. The supernatant liquid was decanted, leaving the precipitated material. This material upon heating at a temperature of 38° to 93°C converted to a hard, brittle composition which broke with conchoidal fracture. The material was soluble in acetone, ethyl acetate, alcohols, and similar solvents. The composition also degraded when the material was placed in water.

Acids that have been polymerized include the herbicides 2,4-D, 2,4,5-T, Silvex, Dicamba, and Picloram (*1*). Others, without appreciable biological activity, include benzoic acid, acetic acid, stearic acid, salicylic acid, tartaric acid, and adipic acid. The rate of degradation can be decreased by heating the polymer, which increased its molecular weight and its hardness. The rate of degradation can also be controlled by varying the surface-to-volume ratio. Hydrophobic acids, such as stearic acid, slow the rate at which degradation occurs.

Initial emphasis has been placed on herbicidal uses for the polymers. Pollution of water supplies commonly accompanies the application of herbicides at useful concentrations. Rain or irrigation water washes away much of the herbicide; hence an overapplication by an order of magnitude is required for effective control. Furthermore, several additional applications per year are needed to maintain the herbicide concentration at an effective level. Polymerized 2,4-D and iron at a rate of 1 pound/acre (1.12 kg/ha) has given exceptional control of weeds in field tests on grazing lands in Kansas, and the control continues for more than 1 year. In other tests control of ironweed and Canadian thistle has been achieved. Further, no evidence for migration of herbicide was found, despite the sloping terrain and heavy rains (*4*).

The increase in efficiency for control of resistant plant species suggests that the concentration of herbicide at the root level is enhanced. This may be due in part to the hydrous ferric oxide gel, which minimizes leaching of the herbicide. Some applications were made from an acetone solution, and others were coated onto granules of diatomaceous earth which were then scattered onto the ground.

In the management of grazing land it is essential that the herbicide not be ingested by animals. The use of granules is an effective way of controlling herbicide ingestion, as they fall to the ground.

Preemergent soil treatment with a wide variety of herbicides and other agents is now possible with the advent of controlled release. The slow release of herbicides has been coupled with beneficial fertilization. Deliquescent 10-30-0 fertilizer prills (*1*) have been coated with polymer, and the fertilizer release was spread over several weeks.

These polymers are expected to improve the effectiveness of defoliation techniques. When sprayed as a solute in an organic solvent, the defoliant forms a sticky resin which clings to foliage. Even heavy rain does not appreciably wash it off. Hence, it is expected to stay where it is placed and do its job, with minimium runoff pollution of water supplies. It is expected that the amount of defoliant required can be reduced by an order of magnitude, with corresponding savings in money, time, and ecological upset.

Medical applications can also be expected. Benign polymeric formulations will be sought as encapsulating materials for pharmaceuticals, such that a slow release can be achieved by way of an implant.

These polymers have appreciable structural strength. As packaging for dry materials, or, with liners, for aqueous materials, the water-degradability feature is highly desirable. As an alternate to the use of nondegradable liners, a local cross-linking at exposed surfaces may impart an extremely slow rate of degradation. When the container is broken, the more readily degradable material will be exposed to moisture.

This wide class of water-degradable polymers offers great promise for the controlled release of herbicides, insecticides, nematocides, slimicides, fungicides, rodenticides, defoliants, and pharmaceuticals. They may also find utility in the packaging industry, since they speedily break down after use.

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### References and Notes

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## Immunoglobulin M Heavy Chain Disease: Intracellular Origin of the Mu Chain Fragment

*Abstract.* *Cells obtained from a patient with mu heavy chain disease synthesize a mu heavy chain fragment with a molecular weight of 55,000. The fragment is detected intracellularly after short labeling times and then is assembled inside the cell and secreted as a disulfide-linked polymer.*

Mutations in bacteria which result in the production of incomplete polypeptide chains have provided models for elucidating the mechanisms governing protein synthesis. Similar aberrations are notably rare in mammalian cells. Therefore the possible occurrence of such an abnormality of human immunoglobulin synthesis is of great interest. The secretion and structure of naturally occurring fragments of the $\gamma$ and $\alpha$ heavy chains have already been described (*1*).

The serum of a patient with chronic lymphocytic leukemia was found to contain both a fragment of the immunoglobulin M (IgM) $\mu$ heavy chain and free kappa light chains (*2*). We now report the results of our study of the intracellular origin of the $\mu$ fragment, the kinetics of its synthesis, its assembly into polymers, and its secretion. The cellular origin of the fragment and the structure of light chains have been described (*3*).

Immunoglobulin-producing cells were obtained when the patient required surgery for repair of a pathologic fracture of the right femur. The cells were immediately suspended in Eagle's minimal essential medium except that it contained only one-twentieth the usual con-