Halley's Whiskers: First Space Polymer Detected

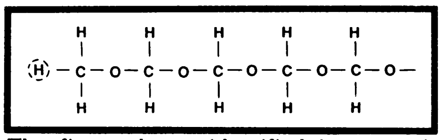
Over the last half-century, radiotelescopes and other earth-based tools have revealed the presence of more than 60 different kinds of molecules in space, plus nearly as many of their isotopic variations. They have ranged from simple molecular hydrogen (H_2)—composed of two atoms of the most ubiquitous element in the universe — to increasingly complex forms such as ethyl alcohol (CH_3CH_2OH) and cyanodecapentyne ($HC_{11}N$). Yet all have been found as individual molecules, never as the kind of linked, molecular chains well known on earth as polymers.

Now, however, one of the results of last year's multi-national, multi-spacecraft encounter with Comet Halley has turned out to be the first identification of a polymer in space. The find is based on measurements from the European Space Agency's Giotto craft, which went closest of all to the comet as the first European space mission ever to get beyond earth-orbit. The substance appears to be the polymeric form of formaldehyde [$(H_2C0)_n$], also known as polyoxymethylene, or POM.

The polymer was identified by Walter F. Huebner of Los Alamos (N.M.) National Laboratory, now on leave at the Southwest Research Institute in San Antonio, Tex. Huebner analyzed the atomic masses of ions detected during Giotto's approach to the comet by an instrument called the positive ion cluster composition analyzer. What the device had measured was a succession of spectral peaks whose regular, alternating pattern seemed to show a mass of 14, then a mass of 16, then 14 again, then 16, then 14 — like a chain with one link consisting of an oxygen ion, followed by an ionized group comprising two atoms of hydrogen and one of carbon, then another oxygen ion and so on. This is the "signature" of POM.

Though it is the first such identification in space, the find was not entirely unexpected. In 1969, ordinary "monomeric," or nonchained, formaldehyde (H_2CO) had become the seventh addition to the list of known "space molecules," and within five years it had been detected in more than 100 interstellar clouds. On earth, the polymer had been synthesized as long ago as the turn of the century, and in 1974, N.C. Wickramasinghe of University College, Cardiff, in Wales, proposed on the basis of his own and others' studies that POM was a natural candidate to exist as an interstellar polymer.

He maintained that it could condense onto silicate grains in space, of the sort ejected by cool, giant stars, and that with the grains at temperatures below about 20 kelvins (-253°C), the result would be



SCIENCE

The first polymer identified in space is shown by this length of the molecular "chain" of polymerized formaldehyde, $(H_2CO)_n$. It was identified from ion-mass spectra measured by the Giotto spacecraft on the way through the coma of Comet Halley. The chain's free ends could bond with various species, such as the hydrogen atom in the dashed circle.

"polymerization into chains." Reporting in the Dec. 6, 1974 NATURE, Wickramasinghe concluded that "POM grains must clearly be regarded as a strong candidate for the main component of interstellar dust."

The new find supports the view of many scientists that comets are repositories of some of the most primitive material in the solar system. Huebner notes in the Aug. 7 SCIENCE that "since POM is still being released from the comet, it appears that the dust that contains POM is also deep in the interior of the nucleus. The POM must have been created in interstellar space, the presolar nebula or the solar nebula and was then incorporated into the cometesimals [particles from which the comet formed] at the time of their formation."

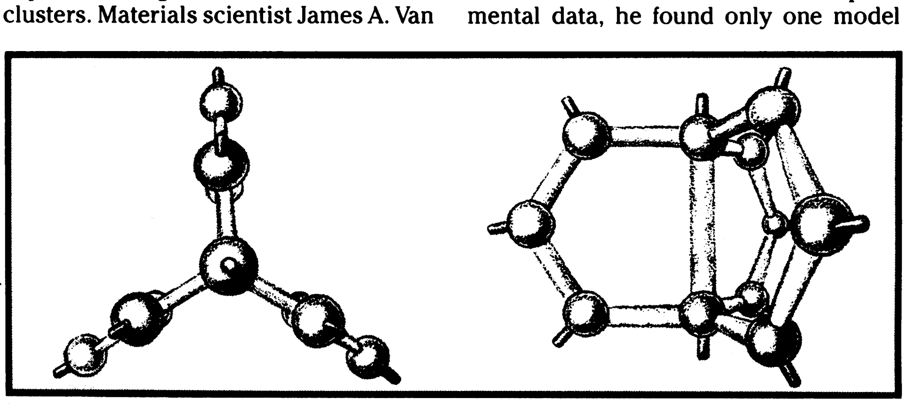
POM may also have played a role in one of the more surprising findings revealed in the photos taken by Giotto and the two Soviet Vega spacecraft that also took part in the encounter: the surprising darkness of parts of the nucleus, which was expected to be ice-bright throughout. It is unclear just how long the POM polymer chains coming from the nucleus actually were, but relatively short ones, says Huebner, tend to attach themselves to grains of carbon or silica in thin, "whisker-like" structures. If these grizzly particles fall back onto the nucleus, he suggests, they could trap incoming sunlight in the spaces between whiskers, scattering it in different directions rather than reflecting it brightly as would a smoother ice "complexion." — *J. Eberhart*

Explaining carbon-cluster magic numbers

When graphite is vaporized by a laser, the liberated carbon atoms are found to be clumped together in remarkably specific numbers: If more than 40 atoms make up a cluster, then an even number will be in the clump, while in smaller clusters, certain "magic numbers"— 11, 15, 19 and 23 — are most common. For years chemists have debated the origin and structure of these clusters, especially those in the 40-plus range. To explain the high prevalence of C_{60} clusters, for example, some researchers have proposed a soccer-ball-like structure called buckminsterfullerene (SN: 11/23/85, p.325).

Now two scientists at Oregon State University in Corvallis have come up with a carbon structure that they believe may explain the magic numbers of the smaller clusters. Materials scientist James A. Van Vechten and chemist Douglas A. Keszler also suggest that their new structure could form the basis of a novel and industrially important material that would have all the strength of graphite, but none of its brittleness. Their work will appear in the Sept. 15 PHYSICAL REVIEW B.

Van Vechten and Keszler happened upon the structure when they were analyzing fine "whiskers" of carbon that they had made by "sputtering" or bombarding a graphite target with ions. Transmission electron microscopy revealed that the whisker material is crystalline, but that the carbon atoms in it are arranged in neither a diamond's nor graphite's pattern. Van Vechten says that after spending months thinking up atomic arrangements that could be reconciled with the experimental data, he found only one model



Van Vechten/Physical Review B

Two views of the proposed 11-atom paddle-wheel structure.